Characterization of Nickel-Ferrite Nanopowder Obtained by Chemical Coprecipitation

Dragoş-Viorel Brezoi, Rodica-Mariana Ion, Gheorghe Ioniţă

Universitatea Valahia, Bd. Carol I, nr 2, Târgovişte
e-mail: dragosh_brezoi@yahoo.com

Abstract

This work aims to analyze the properties of nano-sized nickel-ferrite powder obtained by chemical coprecipitation. Some analytical techniques as: X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometery (VSM) and UV-Vis absorption diffuse-reflectance spectroscopy have been used to characterize the nickel-ferrite powder obtained.

Key words: *nickel-ferrite, coprecipitation, nanoparticles.*

Introduction

The normal crystal structure of spinel (AB_2O_4) consists of the A^{2+} ions occupying all of the tetrahedral coordination sites and the B^{3+} ions occupying all of the octahedral sites of O^{2-} anion's FCC crystal structure [1,2].
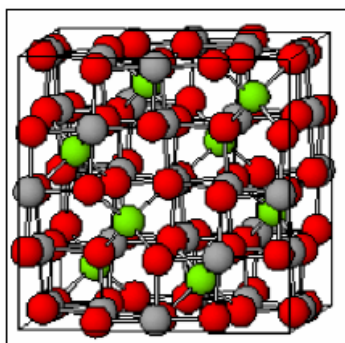
Fig. 1. Crystal structure of $NiFe_2O_4$ where: Fe^{3+} (green), Ni^{2+} (gray), and O^{2-} (red)

In the case of $NiFe_2O_4$, the crystal structure (Fig. 1) is inverse spinel type: Ni^{2+} cation occupies one half of the octahedral coordination sites and half of the Fe^{3+} cations occupy the other half of the octahedral coordination sites as well as all of the tetrahedral coordination sites.

$NiFe_2O_4$ has recently been studied as a component for ferrofluids that are colloidal suspensions of super-paramagnetic nanoparticles. Super-paramagnetism occurs when ferromagnetic particles have a critical size around 10 nm (the particle's diameter is less than a single magnetic domain)

[3]. In the case of nanoparticle systems, each particle can spontaneously switch the magnetic orientation like a single domain [4].

Experimental

A wet chemical method was adopted to prepare the nickel-ferrite nanopowder. We have used: nickel chloride heptahydrate $NiCl_2 \cdot 7H_2O$, ferric chloride anhydrous $FeCl_3$, sodium hydroxide anhydrous $Na(OH)$, and oleic acid $C_{18}H_{34}O_2$, all were purchased from Aldrich and Merck. In all experiments it has been used distilled water. The experimental conditions are: temperature was kept constant at 70 ^{o}C, stirring 45 minutes, and pH = 11. We prepared a mixed solution with 6,4884 g $FeCl_3$ and 5,61398 g $NiCl_2 \cdot 7H_2O$ in 200 ml distilled water and another solution of 12 g NaOH dissolved into 100 ml distilled water (precipitation agent):

$$2FeCl_3 + NiSO_4 + 8NaOH \xrightarrow{70\,^{o}C} 4H_2O + Na_2SO_4 + 6NaCl + NiFe_2O_4\downarrow \qquad (1)$$

Then, it was added few drops of oleic acid (OA) like surfactant into the nickel-ferrite suspension already prepared, and sonicated at 40 % amplitude for 25 seconds. Due to the presence of the surfactant oleic acid (OA), the particles will be covered by a protection layer during the mixing process and minimize the agglomeration tendency of nickel-ferrite nanoparticles. The precipitate was decanted with a permanent magnet and washed with distilled and deoxygenated water. The nickel-ferrite was dried in an oven at 80 °C until it's formed a fine powder without water and oleic acid (Fig. 2).

Fig. 2. The nickel-ferrite powder obtained

Some analytical techniques as: X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometry (VSM), and UV-Vis absorption diffuse-reflectance spectroscopy, have been used to characterize the nickel-ferrite powder obtained.

Results and Discussion: Properties of Nanoparticles

Morphology and phase

In fig. 3 is shown the XRD spectrum for nickel-ferrite powder sample. We have used Scherrer's equation applied on the most representative peak at $2\Theta = 36$ degree, to calculate average size for the nickel-ferrite particles:

$$d = k\lambda \, [L_{1/2} \cos \Theta]^{-1} \qquad (2)$$

where *d* is the particle's average diameter, $k = 0.9$, $\lambda = 1.5418$ Å (for CuKα X-Ray source at 35 kV), Θ - peak position and $L_{1/2}$ – effective full width half maximum of peak at 2Θ = 36 degree. It was calculated the average diameters of particles and this was 12 nm.
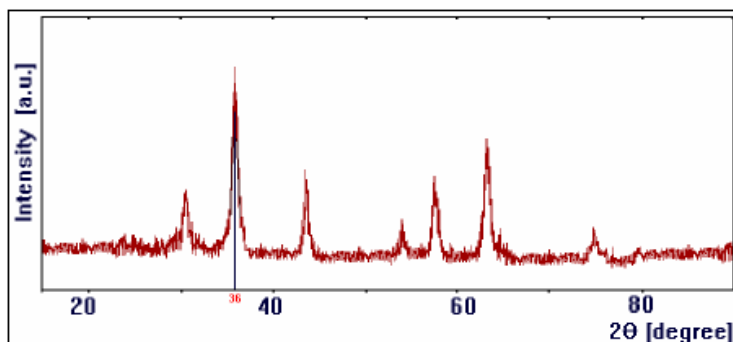

Fig. 3. XRD spectrum of the sample powder of nickel-ferrite

We have realized TEM imaging to validate the results regarding average size of nickel-ferrite particles.
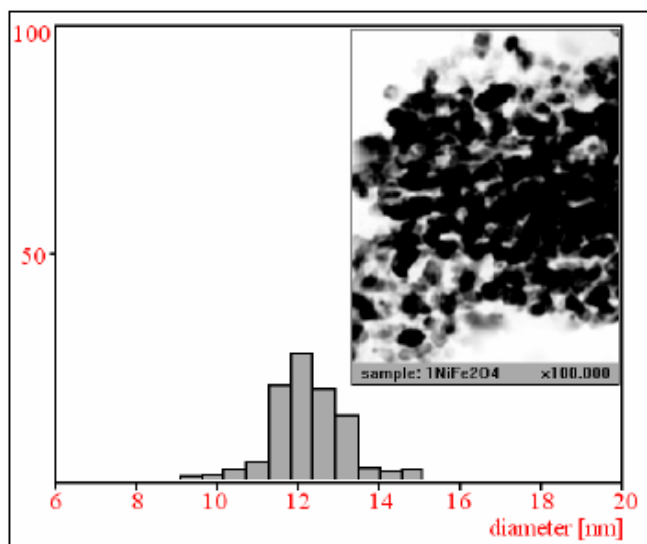

Fig. 4. TEM image of the sample of nickel-ferrite powder and the particle's size distribution

The TEM image of the sample of nickel-ferrite powder (Fig. 4) clearly shows that the nanoparticles are polydisperse with diameter in the range 9 – 15 nm. The particles have low tendency to agglomerate.

UV-Vis absorption diffuse-reflectance spectroscopy

UV-Vis spectroscopy is used in the quantitative determination of transition metal ions. Transition metal ions can be coloured (i.e., absorb visible light) because *d* electrons within the metal atoms can be excited from one electronic state to another. The colour of metal ion is strongly affected by the presence of other species, such as certain anions or ligands.

A simple diffuse reflectance UV-Vis spectroscopic determination was developed. In contrast to common metallic oxides, like hematite (α-Fe_2O_3), double metallic oxides exhibit well-structured characteristic absorption peaks which allow their recognition.

Diffuse reflectance spectroscopy and its application to study metal oxides have been reviewed recently [6]. Briefly, this technique is based on the reflection of light in the ultraviolet (210–420 nm), visible (420–700 nm) and near-infrared (700–2500 nm) regions by a powder sample. In a diffuse reflectance spectrum (DRS), the ratio of the lights scattered from *a* (> 2–3 mm) thick layer of sample and an ideal non absorbing reference sample is measured as a function of the wavelength λ. DRS has been used extensively to study transition metal oxides to obtain information on surface coordination and different oxidation states of metal ions by measuring *d–d*, *f–d* transitions and oxygen–metal ion charge transfer bands. However, this technique has limitations due to the difficulty in interpreting the large bandwidths and specular reflectance often observed in the spectra.
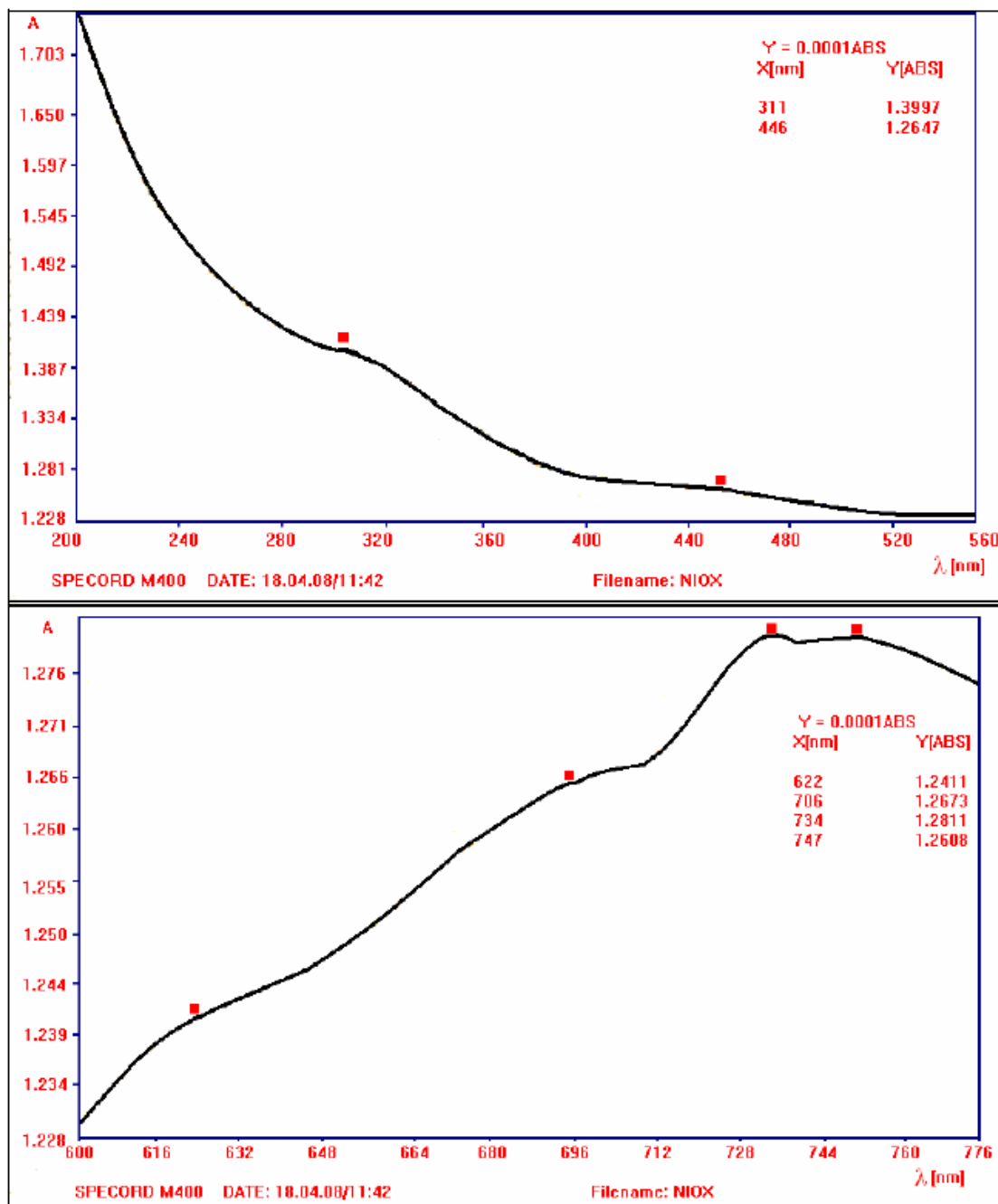

Fig. 5. UV-Vis absorption diffuse-reflectance spectrum of nickel-ferrite nanopowder

UV-Vis absorption diffuse-reflectance spectrum of nickel-ferrite (Fig. 5.) show absorption band in the 300-500 nm region (311 and 446 nm), where clearly appears the CT transition d-d bands corresponding to Ni^{2+} and Fe^{3+} with octahedral symmetry in $NiFe_2O_4$ [5].

In the nickel-ferrite, the Ni^{2+} cation occupies one half of the octahedral coordination sites. In the 500-800 nm region, the bands (622, 705, 734, 747 nm) corresponding to cations with tetrahedral symmetry in $NiFe_2O_4$ appears.

Magnetic properties

We have determined typical magnetic properties on the solid sample of nickel-ferrite powder mixed with PVA and pressed into pellets. All VSM measurement was made at room temperature.

A bulk nickel-ferrite is ferromagnetic but a nanoparticles is possible to be superparamagnetic because the average diameter is 12 nm. Typical magnetic properties determined with VSM at room temperature are: saturation magnetization $M_s = 37.7$ emu/g, remanent magnetization $M_r = 5.6$ emu/g, coercivity field $H_c = 60$ Oe. The magnetization curve is shown in the Fig. 6. These nickel-ferrite nanoparticles show a weak tendency to become superparamagnetic.
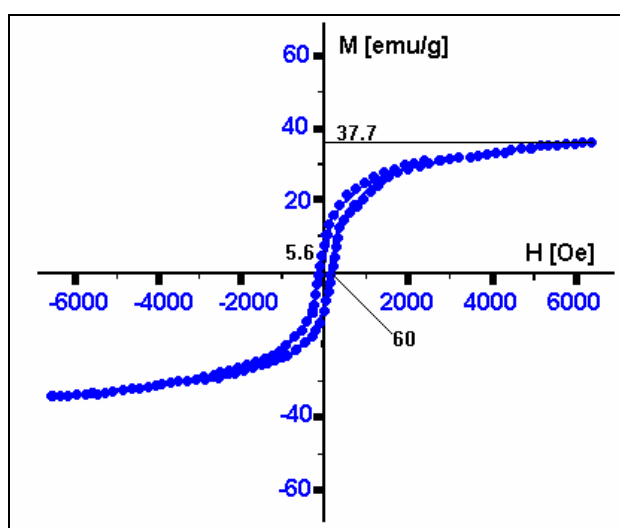

Fig. 6. Magnetization curves for nickel-ferrite sample

Conclusions

It was obtained nickel-ferrite nanoparticles by chemical coprecipitation using nickel chloride heptahydrate, ferric chloride anhydrous, sodium hydroxide anhydrous (precipitation agent), and oleic acid (surfactant), at low temperature.

Some analytical techniques as: X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnetometery (VSM) and UV-Vis absorption diffuse-reflectance spectroscopy have been used to characterize the nickel-ferrite powder obtained.

For powder sample of nickel-ferrite, the measured values of properties are shown in Table 1.

Table 1. The measured properties of nickel-ferrite powder sample

Sample	d [nm]	M_s [emu/g]	M_r [emu/g]	H_c [Oe]
$NiFe_2O_4$	12	37.7	5.6	60

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Caracterizarea nanopulberii de ferită de nichel obţinută prin coprecipitare chimică

Rezumat

Scopul acestei lucrări este de a analiza proprietăţile feritei de nichel sub formă de pulbere obţinută prin coprecipitare chimică. Caracterizarea nanopulberii de ferită de nichel s-a realizat prin: difracţie de raze X (XRD), microscopie electronică prin transmisie (TEM), magnetometrie cu probă vibrantă (VSM) şi spectroscopie de absorbţie în UV-Viz.